Review: National Laboratory Sensor Projects for CIDI/SIDI Engines

DOE Workshop on Sensors for Fuel Cells and CIDI/SIDI Engines

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

Presentation Outline

- Vehicle exhaust gas constituent sensors being developed under DOE CRADA 94-MULT-912-ES (LANL, LLNL, ANL, and SNL with USCAR/LEP)
- Other gas sensor technology development at the National Labs
  - NOx, CO, HCs, O_2, H_2
- Other sensor developments for engine systems
  - Particulate counters
  - Pressure monitors
  - Fuel vapor sensors
  - Fluid monitors
  - Rotation/position sensors

LANL Sensor Development

Fernando Garzon- Project Leader, Eric Brosha, R. Mukundan and David Brown -Technical Staff

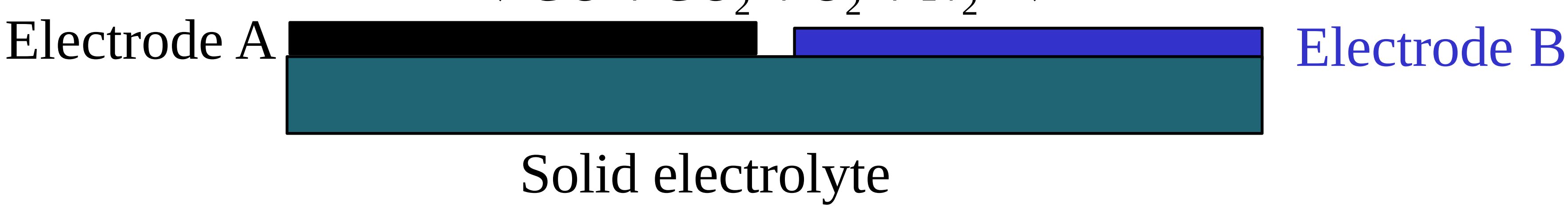
- Goal - develop with USCAR new ceramic sensors that measure hydrocarbons/carbon monoxide directly
- Electrochemical ceramic sensors capable of *insitu* operation (temperatures from 400-900 C)
- All new autos use ceramic zirconia sensors -proven technology
- Good sensitivity and fast response
- Simple transduction voltage or current electrical signal
- Ease of sensor fabrication and detector system implementation "spark plug" type device
- Fast light off -micro-sensors can be self-heated

LANL Sensor Development Cont.

- A non-equilibrium potential develops at an electrode in the presence of reducing-gases
- Detect reducing-gases (H_2, CO, hydrocarbons, NO_x) in an oxygen containing stream
- Mixed Potential is fixed when the rates of the reduction and oxidation reactions are equal
- The Mixed Potential is different on dissimilar catalytic electrodes
- Potential difference between electrodes A and B is sensor response

$$\frac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e^{'} \leftrightarrow O_O \qquad CO + O_O \leftrightarrow CO_2 + V_O^{\cdot\cdot} + 2e^{'}$$

$$\rightarrow CO + CO_2 + O_2 + N_2 \rightarrow$$



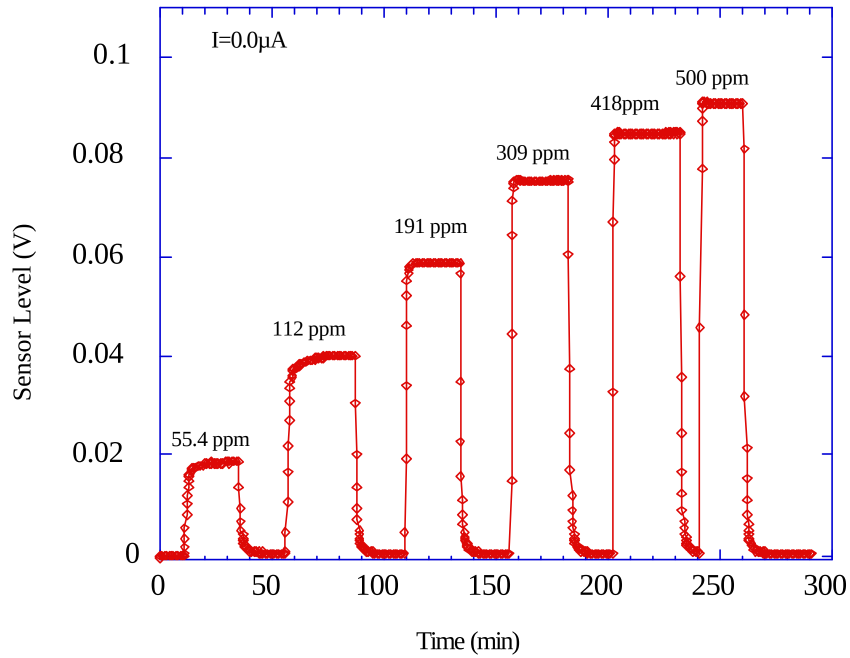
LANL Sensor Development Cont.

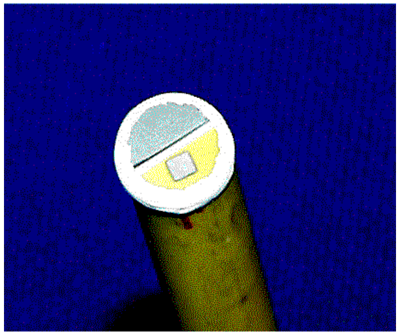
•LANL sensors show fast reproducible responses to hydrocarbons such as propylene

•Long term stability and durability- over 3000 hours of laboratory testing under simulated exhaust gas mixtures

•Ongoing engine testing with USCAR for use as OBD II sensors

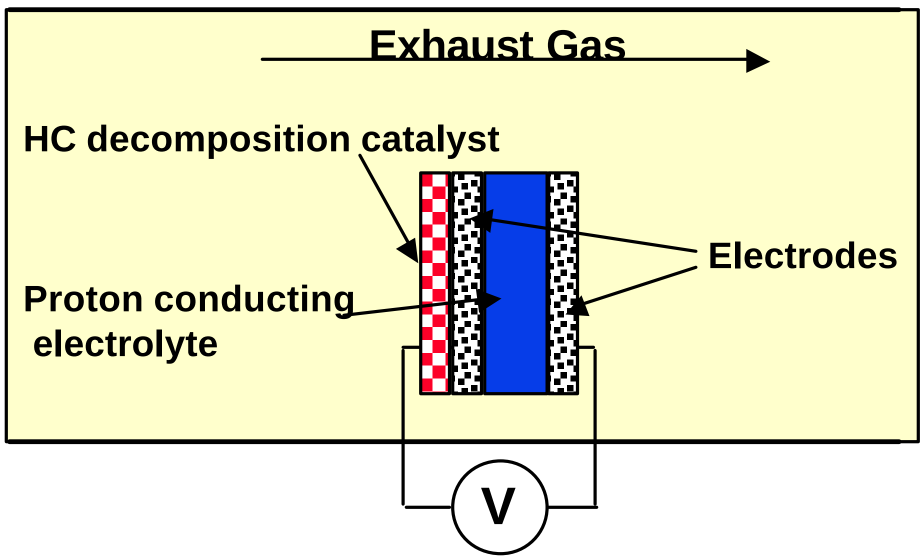
•Patent applied for sensor technology





3 electrode device mounted onto a ceramic tube with a glass seal

At Lawrence Livermore National Lab, we are developing solid state electrochemical sensors for HC emissions monitoring



Principle of operation: this is a catalytic versus non-catalytic sensing mechanism. Various catalysts can be used to decompose HCs to hydrogen. The excess hydrogen concentration is detected by the hydrogen sensor.

Advantages:
- simple
- robust
- low cost
- can be very selective

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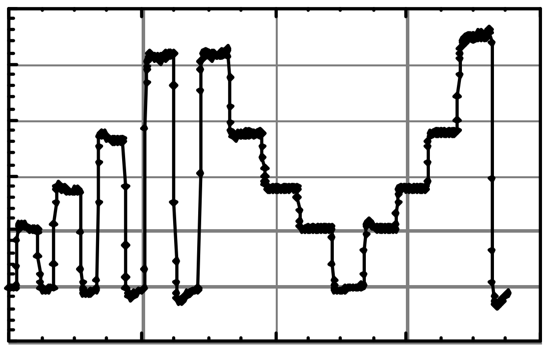
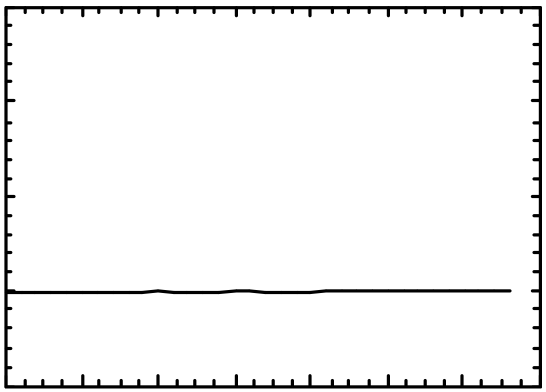
Characteristics of LLNL HC sensor

Sensor response to C_2H_6



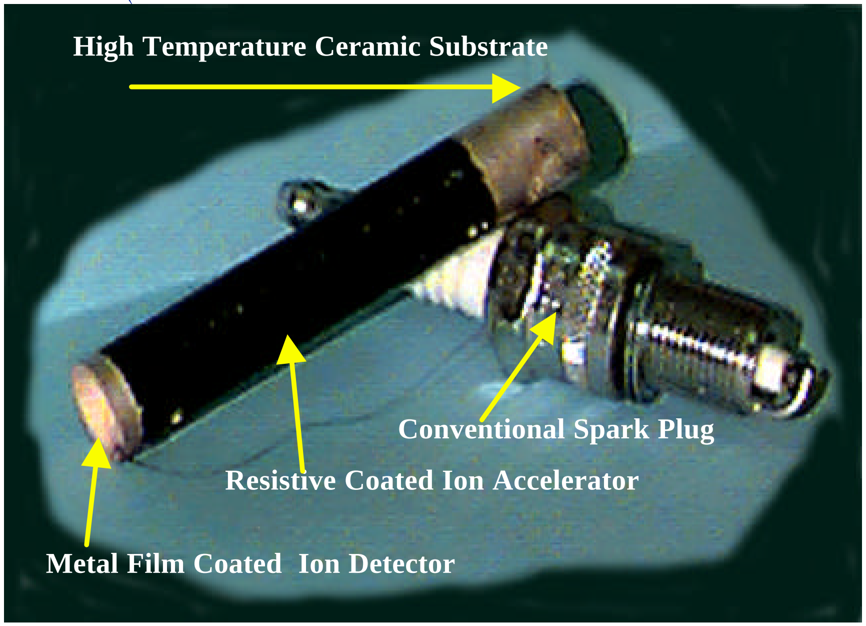
Sensor response to CO

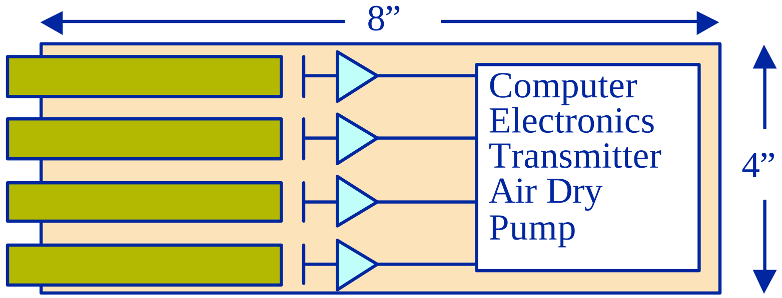


- sensor responds to various HCs in both lean and rich conditions
- no drifting
- response time is less than 5 s
- absolute selectivity versus H_2 and CO
- no flow rate dependence
- weak temperature dependence
- some oxygen dependence

The first generation sensor has been submitted to dynamometer test at Ford Research Lab

Exhaust HC Ion Mobility Sensor





Chemical Selective Membranes

Description:

- Miniaturized intelligent ion mobility sensor array incorporates chemically selective membranes.
- Multiple chemically selective membrane inlet system provides enhanced specificity over conventional IM system.
- Capable of analyzing samples from semivolatiles, and volatiles without preparation with high sensitivities.

Applications:

- Land Mine detection
- Explosive detection
- Troop security
- Clandestine or covert operations
- Cooperative treaty monitoring
- Law enforcement support
- Chemical weapons detection
- Detection of nuclear proliferation activities/facilities

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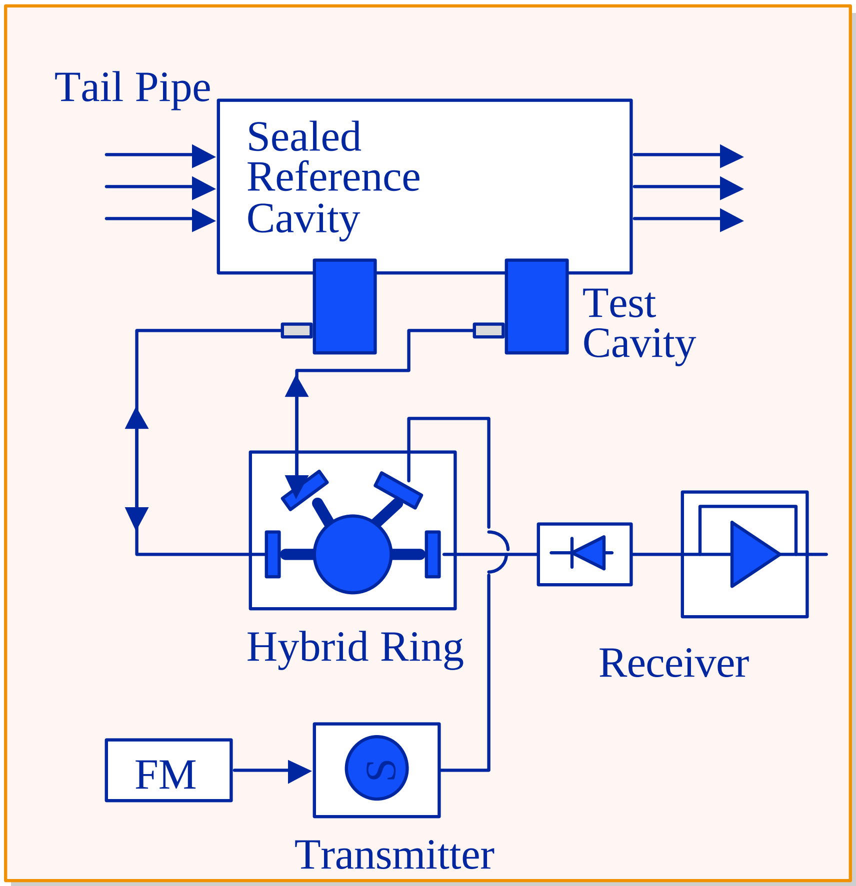
Microwave Sensor for Bulk Measurement of NOx



Description:

- Based on microwave rotational absorption of dipolar gases
- Uses low-cost, compact cavity or microstrip resonators to increase effective absorption path lengths
- Differential sensing with dual sensors allows robust measurements
- Frequency range is selected to maximize NOx absorption
- Immune to particulates or sulfur contamination on the sensor
- Natural discrimination to nonpolar gases like methane and CO_2

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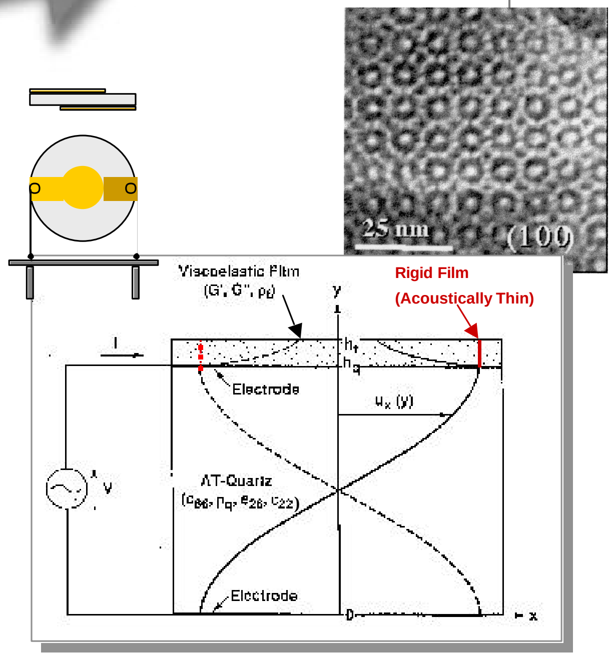
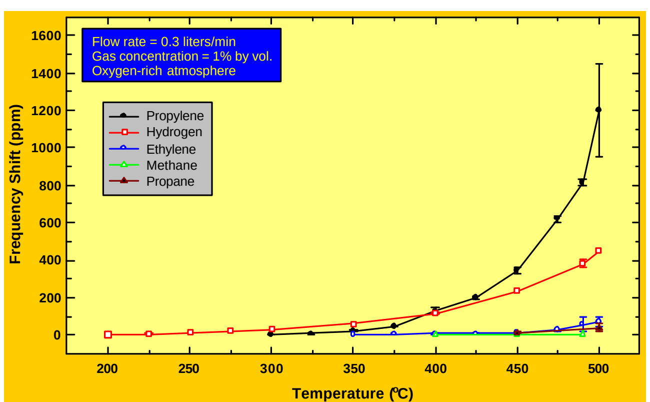
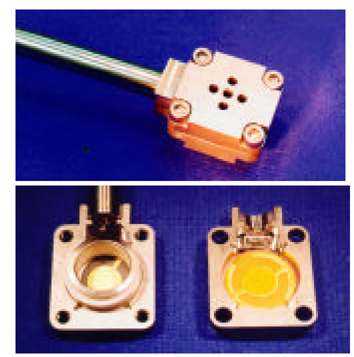
SNL Acoustic Wave HC Gas Sensor



- Sensor consists of AT-cut quartz TSM resonator with catalytic-metal-doped porous silica thin film on surface.
- CTAB surfactant in sol-gel templates pores and achieves high surface area (> 700 m²/g). Pd doping elicits strong HC response.
- Catalytic combustion of HCs + O_2 in film increases the temperature, stressing resonator surface, and shifting frequency. Response is similar to a calorimeter.
- Operation to ~ 525 °C. Quartz Curie point 573 °C.
- Min. detection limits < 50 ppm [C_3H_6]
  Response time: few seconds
  O_2 dependent response at high conc.
  No cross-sensitivity to CO or NOx
  Small sensitivity to CO_2 and H_2O
- Prototype system being prepared for performance evaluation





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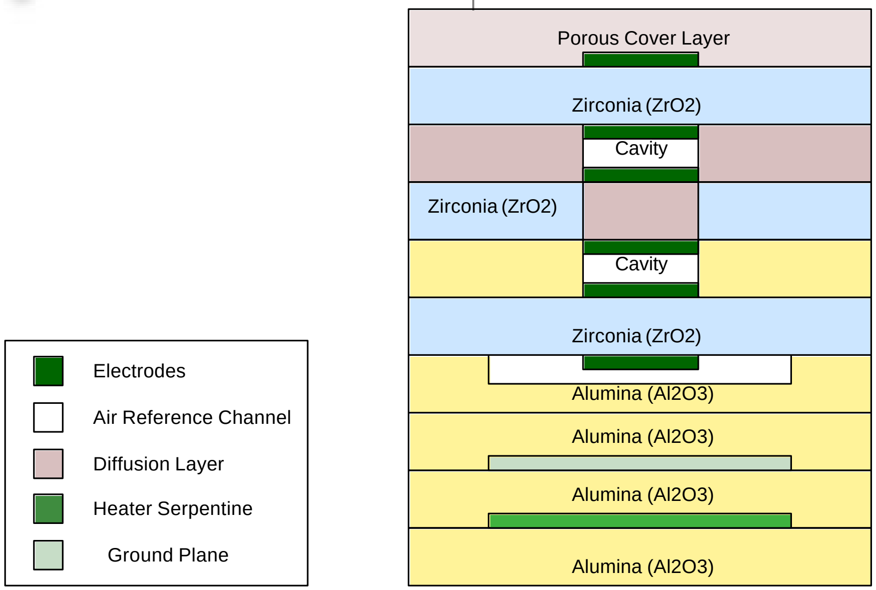
ORNL NOx Sensor



Sensor Type #1 (Gasoline lean burn engine)

Sensitivity: 100-200 ppm (potential lower detection limit for diagnostics)

Accuracy: +/- 20 ppm

Response Time: < 1 sec (0-90% full scale)

NO/NO_2: equally sensitive to NO and NO_2

Concerns: sulphur

Sensor Type #2 (Diesel application with urea)

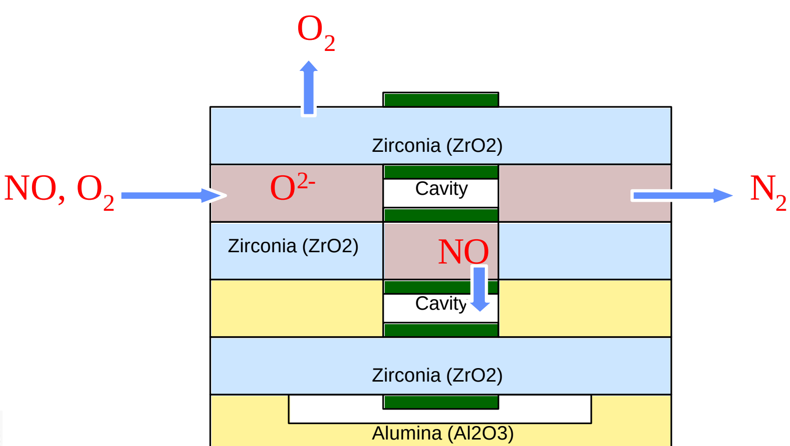
Sensitivity: 20-300 ppm

Accuracy: +/- 20ppm

Response Time: < 1sec (0-90% full scale)

NO/NO_2: separately measure NO and NO_2

Concerns: soot, sulphur and urea(NH_3)



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Accomplishments in PNNL Oxygen and NOx Sensor Development Programs

Development of:

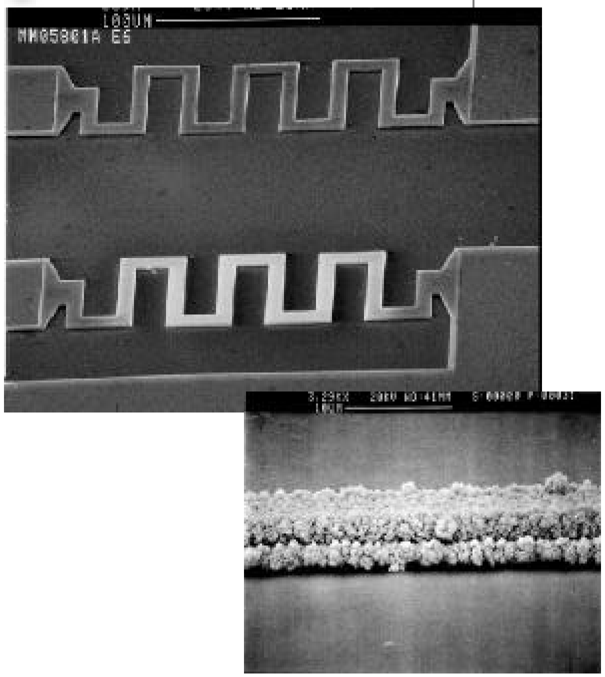
- Aqueous tape casting system
- High electrical resistance barrier layer
- Porous protective layer
- Gas diffusion layer
- Novel selective electrode materials

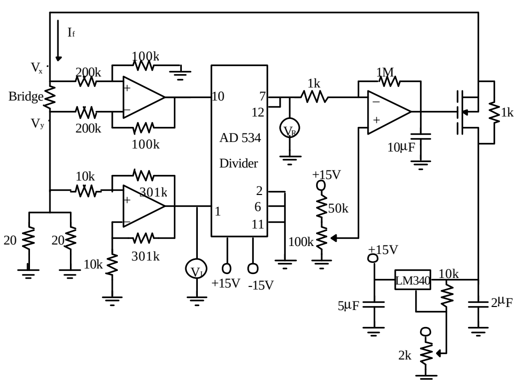
Five year history of materials development, testing and evaluation with OEM and suppliers

PNNL Sensor Capabilities

- Novel materials design and synthesis
- Materials processing (tape casting, tape calendering,…)
- Material Analysis and Characterization
  - Surface (XPS, Auger, SEM, FTIR, Raman)
  - Bulk (XRD, TEM, NMR)
- Sensor testing & evaluation
  - Gas phase (pure gases, simulated exhaust, real exhaust) using FTIR, GC/MS
  - Electrical properties

SNL Micromachined Catalytic Gas Sensor

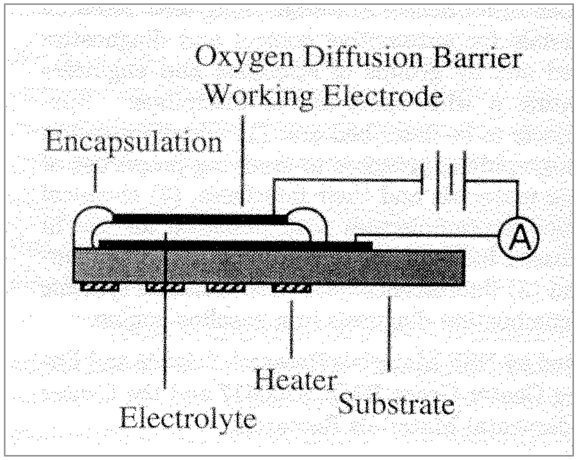




- Suspended polysilicon filaments 2 µm thick, 10 µm wide, and 100 to 1000 µm long
- Micro-CVD deposition of catalytic Pt coating
- Combustible gases (CO, H_2, HCs) react with O_2 on filament, releasing heat
- Constant resistance (temperature) control circuit allows gas concentration to be determined from measured power
- Small suspended filaments allow for efficient electrical heating and isolation
- Dual bridge provides for self-compensating design
- Micromachining allows for batch processing and microelectronic integration
- Applications: natural gas BTU monitor, catalytic converter monitor

Lean-Burn Oxygen Sensors

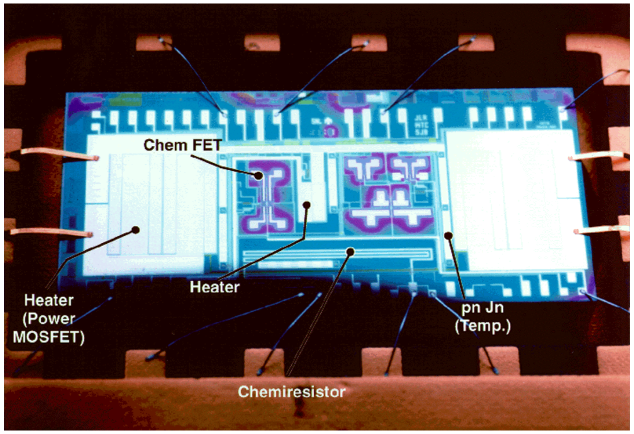
- Zirconia oxygen sensors work well around stoichiometric (air-fuel ratio: 14.8 to 1). Potentiometric response is non-linear (λ shape) with changes in O_2 partial pressure.
- Lean-burn engines require wider dynamic range of O_2 concentrations. Air-fuel ratios > 15
- LANL and LLNL development of linear amperometric O_2 sensors with porous metal oxide or pin-hole aperture diffusion barriers.
- Linear response up to 25% O_2 partial pressure.



LANL linear response oxygen sensor

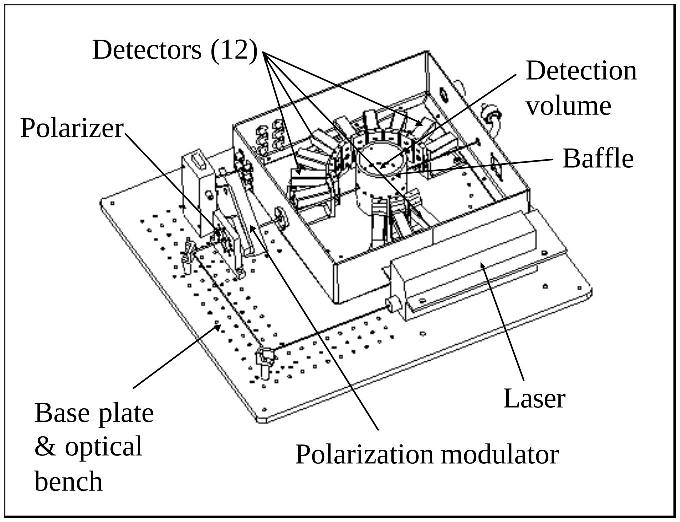
Hydrogen Detectors

- Solid-state catalytic gate (Pd-Ni) FETs [SNL]
- Thin-film Pd-Ni chemical resistor on silicon [SNL]
- Thick-film Pd chemical resistor on ceramic [ORNL]
- Optical fiber with chemochromic thin films [NREL]
- Optical fiber with Pd thin film [SNL]

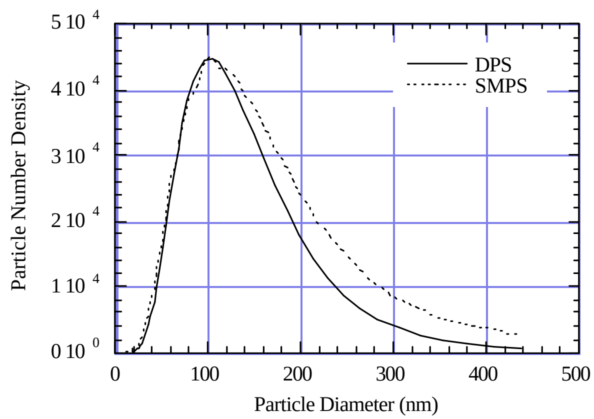


Sandia's robust integrated hydrogen sensor

Diesel Particle Scatterometer (DPS)



- Particulates from newer engines are smaller and more difficult to measure.
- Polarized light scattering provides rapid, accurate, and *in situ* measurement of diesel exhaust particulate characteristics:
  - size, number density, morphology, and optical properties
- DPS used to study variables: engine type, load, RPM, fuel additives, and post-combustion processes



- Simultaneous measurements on Jetta Diesel engine at ORNL using the DPS, and the Scanning Mobility Particle Analyzer (SMPS) - Standard method, but slow
- Demonstrated DPS operation at > 1 Hz data rates

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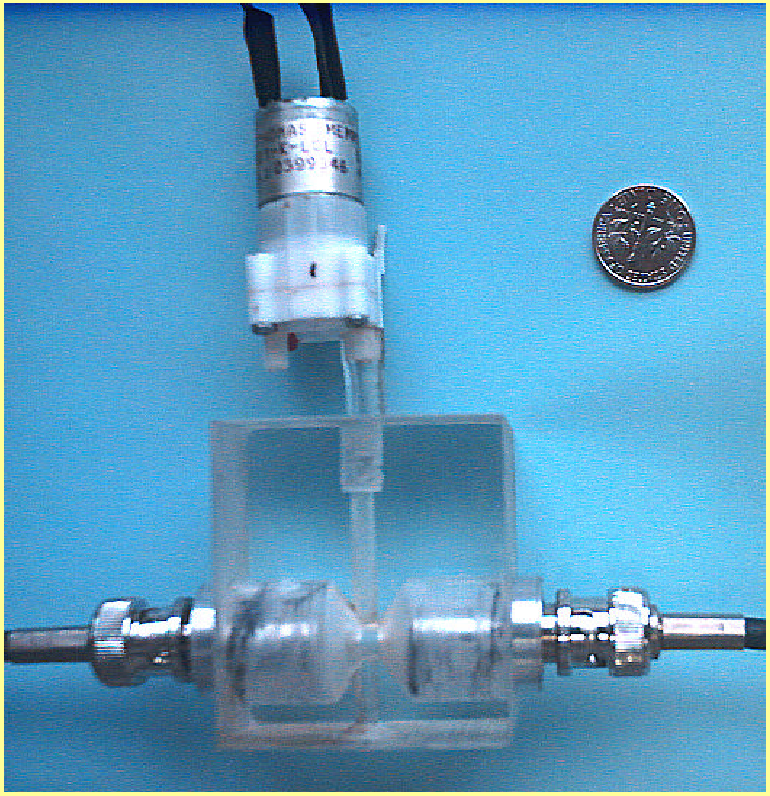
Ultrasonic Particulate Monitor



Description:

The ANL ultrasonic particulate analyzer detects particles/smoke in air by measuring changes in sound velocity and acoustic attenuation. It consists of an acoustic cavity and a pair of piezoelectric transducers operated in a pitch-catch mode.

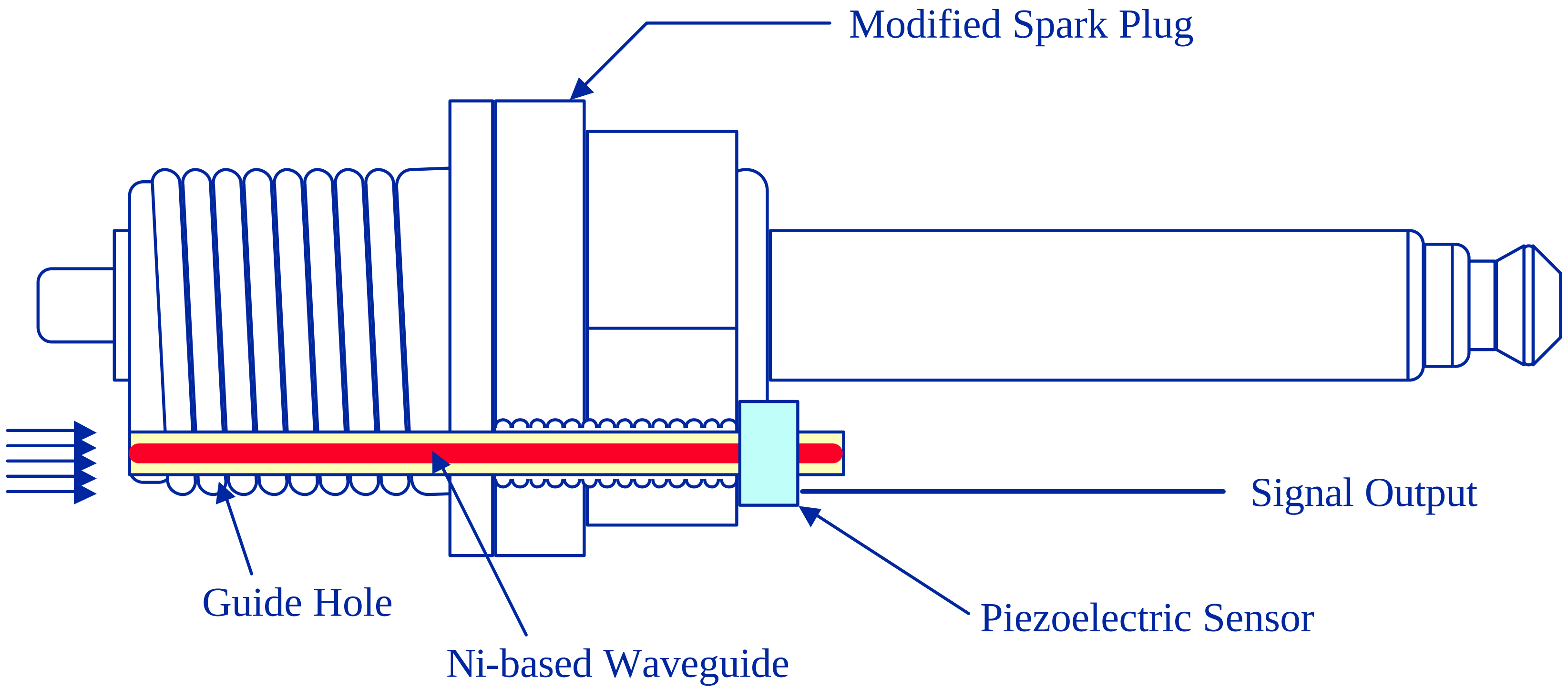
Instrument features:

- Rugged
- Low cost
- Easy operation

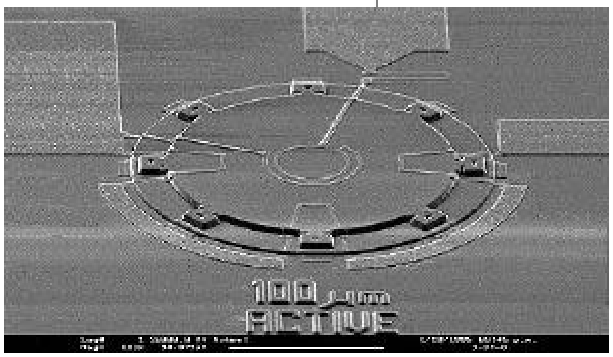
Other Applications:

- Helium/hydrogen leak detectors
- Radon gas detector
- Trace toxic gas detector

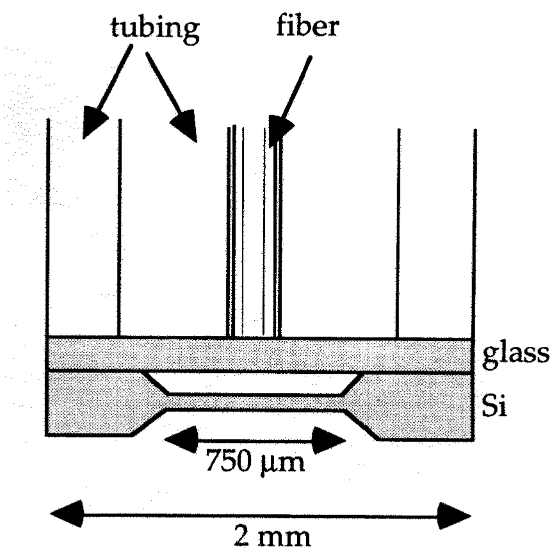
Ultrasonic Sensor for Cylinder Pressure Monitoring



Pressure Sensors



- MEMS pressure sensors [SNL]
- Devices fabricated using bulk (poly-Si) or surface (SiN) micromachining
- Sensing with poly-Si piezoresistors

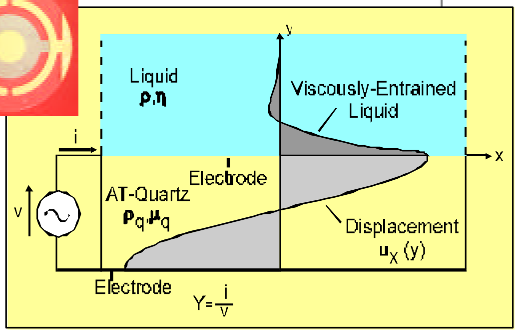


- Optical fiber pressure sensor using micromachined Si membrane [LLNL]
- Fabry-Perot cavity formed by glass plate and deflecting membrane
- Uses LED light source
- Dynamic range to > 1000 psi

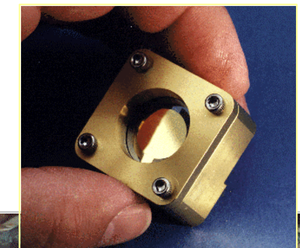
Fuel Composition Monitors

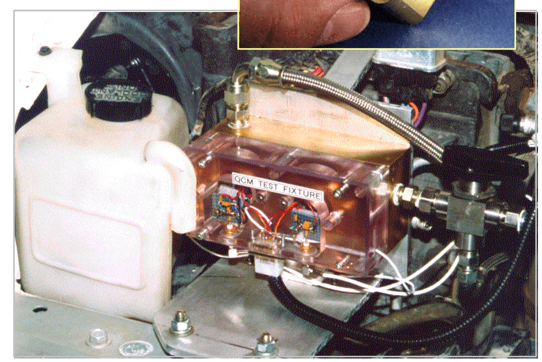
- Chemical sensor arrays detect fuel vapors.
  - Coated acoustic devices or resonant structures: SAWs, QCMs (TSM resonators), FPWs, microcantilevers [SNL, ANL, PNNL, ORNL]
  - Chemiresistors [LLNL, ORNL, PNNL, SNL]
  - ChemFETs [PNNL, SNL]
- Diverse sensor coatings are partially selective to many vapor molecules.
- Pattern recognition algorithms, neural networks, or other chemometric techniques used to identify and quantify vapors.

SNL Oil Viscosity Monitor

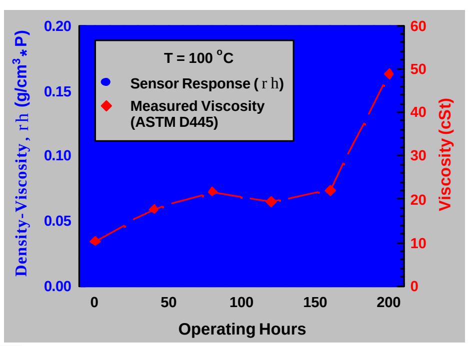


- A thickness shear mode quartz crystal resonator viscously-entrains liquid in contact with the surface
- Shifts in resonant frequency and magnitude are proportional to liquid density-viscosity





- Extracted oil samples can be placed on resonator surface
- Robustly packaged resonators can be mounted in vehicle oil pan or placed in oil flow line
- Tests conducted in laboratory, in engine dynamometers, and in operating vehicles



- Lubricant viscosity increases as oil degrades (oxidation due to high temperatures and pressures)
- Resonator response agrees well with viscosity measured using ASTM techniques (correlation > 0.9)

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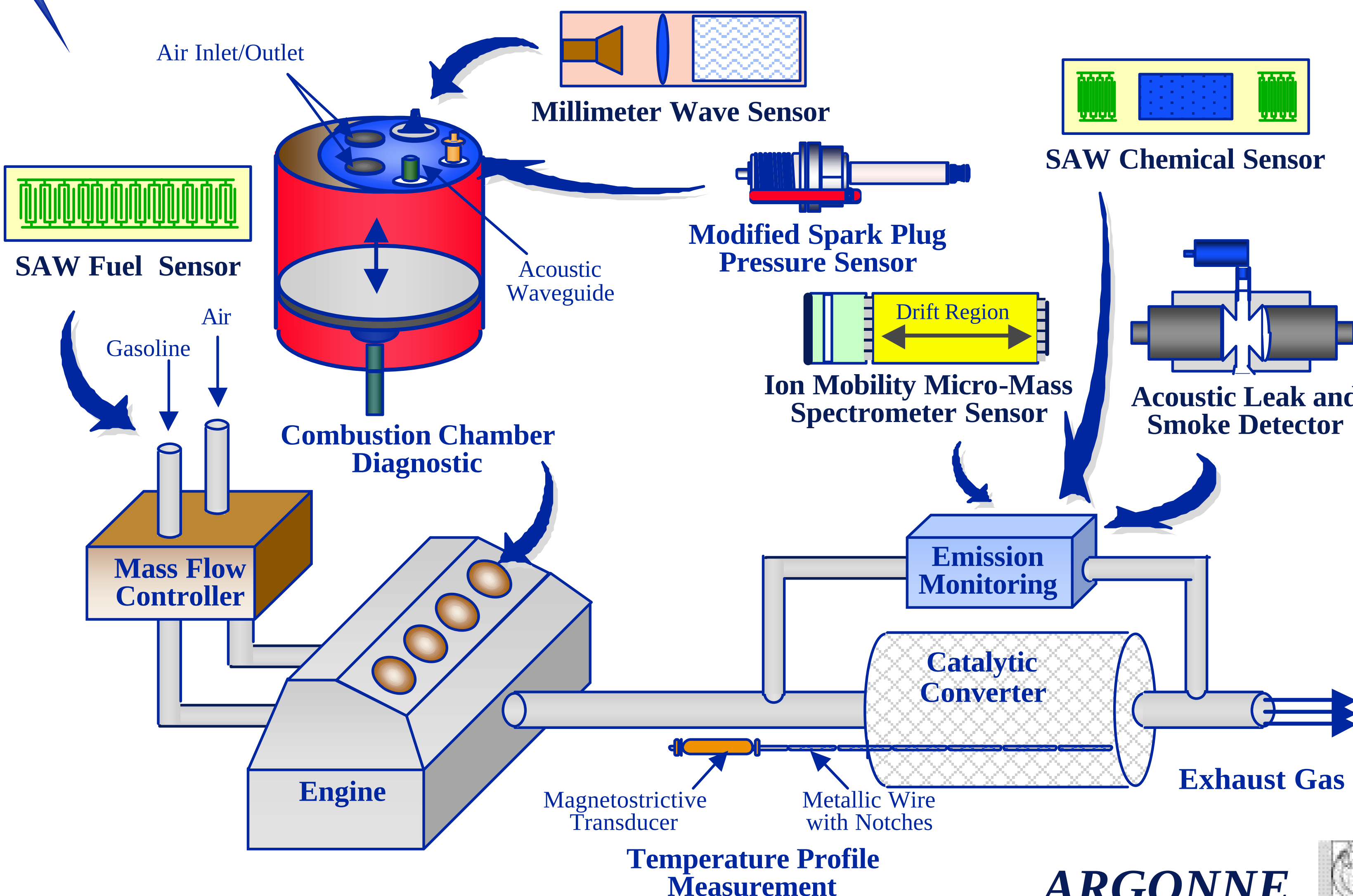
Sandia National Laboratories

Rotation/Position Sensors

- Non-contact rotation and position sensors measure the crankshaft angle, engine rotation speed, and other shaft positions.
- Desire wide linear dynamic range, high resolution (~ 0.1%), low cost, and long life at high temperatures.
- Planar Hall effect devices [SNL]
  – InSb and InAlSb (high m_e) on GaAs substrates
- Giant Magnetoresistance (GMR) field sensors [ORNL]
  – Alternating layers of ferromagnetic and nonmagnetic material
- Rotary differential capacitance transducers [ORNL]
  – Shaped electrodes with 25 μm polyester film dielectric

Total Engine and Exhaust Emission Monitoring



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